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Molybdenum-containing polysalts of the poly[ferricene-1,2(1,3:1,1′)diyl-methylene] cation*

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Poly[ferricene-1,2(1,3:1,1′)diyl-methylene) polycations, generated from the neutral precursor polymer 1 ($\bar{M}_n = 2800$) by dioxygen (O_2) oxidation in sulfuric acid medium, are paired first, in a model reaction, with the hexafluorophosphate anion and, in the principal series of experiments, with the two molybdenum-containing complex anions, octamolybdate and phosphododecamolybdate. The model poly(hexafluorophosphate) 2b, as well as the polymolybdates 2c and 2d, precipitate from aqueous acidic solution of the corresponding polysulfate 2a after anion exchange; scopically. In addition to the hexafluorophosphate anion, the model polysalts 2b contain small proportions, typically 5–15%, of sulfate anion (probably present as HSO_4^-), indicating incompleteness of the anion exchange process. Analytical data suggest similarly incomplete exchange of anions also for the polymolybdates 2c and 2d. Oxidation of ferrocene units along the polymer chain is practically complete in the great majority of polysalts 2 synthesized. The molybdenum-containing polymers are of interest as plant micronutrients possessing slow-release properties.

Keywords: Polyferricene, molybdenum, polymer, polycations, iron, trace elements, plants, micronutrients

INTRODUCTION

Both iron and molydenum are among the ten trace elements essential to all plant life. Iron, in the form of iron proteins and other organic complexes, plays a vital role in photosynthetic electron transfer, nucleic acid metabolism, reduction reactions, and various catalytic processes. The primary function of molybdenum as a redox carrier is found in nitrogen-metabolizing enzyme systems. Although the quantities needed by plants are comparatively low (molybdenum contents of 0.03–0.15 ppm, dry mass, in the tissues of most plants are generally regarded as sufficient to meet the requirements for this element), so are the surface-soil concentration limits above which the elements may show severe phytotoxicity. For molybdenum, for example, this threshold limit is considered to be about 2–10 ppm, dry mass, which should be compared with 'normal' molybdenum contents of 1.5–2.5 ppm typically found in soils. A slow-release process, which would provide for a steady concentration of active nutrient in the soil over a prolonged period of time, replacing conventional single ('one-shot') applications with concomitant risk of overdosing, should lend itself as a novel means of suppressing phytotoxicity and obviating, or at least alleviating, the problem of premature nutrient deactivation in the soil.

As part of a plant micronutrient study in this laboratory, aimed at the development of polymeric carriers capable of slow-release delivery of iron and molybdenum trace elements, interest arose in macromolecular ferricenium salts containing molybdenum in complex anion form. Both ionic behavior, and yet water insolubility, were prescribed by the requirement for a certain degree of hydrophilic character and soil compatibility with concomitant resistance to premature removal from the soil by natural leaching processes. The known[2] poly[ferrocene-1,2(1,3:1,1′)diyl-methylene] **1**,[3] obtainable by Lewis acid-catalyzed polycondensation of *N*,*N*-dimethylaminomethylferrocene, suggested itself as

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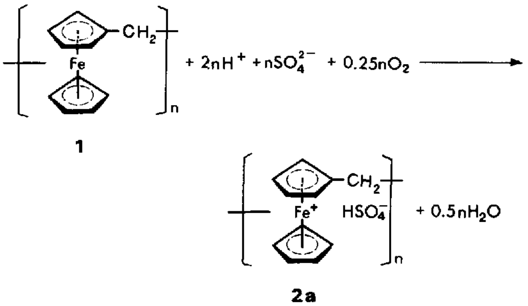
*Metallocene Polymers 44. For Part 43, see Ref. 1.

a candidate base polymer and was selected for this investigation.

RESULTS AND DISCUSSION

The polymer sample of **1**, a fraction with $\bar{M}_n = 2800$, was oxidized in dioxygen-saturated sulfuric acid at room temperature (Eqn [1]) under conditions known[4] to favor ferrocene oxidation. The reaction proceeded smoothly, and the resultant polysalt, a poly(ferricenediyl-methylene sulfate) formulated (without isolation and further characterization) as the hydrogen sulfate salt **2a** (Eqn [1]), remained dissolved in the medium. A minor amount of degraded material, partly depleted in iron content ($C/Fe \simeq 3.35$, as against 2.37 in **1** and **2a**) as a result of metal-ring bond cleavage by the strong acid,[5] precipitated from the sulfuric acid solution and was removed by filtration. The filtrate was diluted with water to a (base molar[6]) polymer concentration of 0.14–0.17 mol dm^{-3}

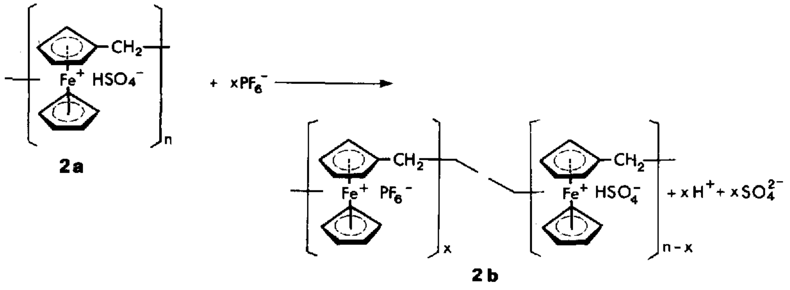
In order to test the precipitability of the polycation by bulky anions of well-defined composition so as to facilitate compositional characterization of the product polymer, the solution of **2a** so obtained was first treated with an excess (two to five equivalents) of ammonium reineckate (ammonium tetrathiocyanatodiamminechromate(III), $NH_4[Cr(NH_3)_2(SCN)_4]$). The results of these model experiments were disappointing; although smoothly precipitating, the polycations obtained possessed highly erratic elemental compositions because of anion complex degradation under these conditions and were, therefore, not further investigated.[7] More promising proved the precipitation with excess ammonium hexafluorophosphate. The polysalts precipitating in 85–95% yields were found to be copolymers possessing hexafluorophosphate salt repeat units as the majority component, with minor proportions of unchanged hydrogen sulfate salt units present in the backbone (Eqn [2]; random placement of repeat units implied in this and subsequent representations).



[1]

The content of sulfate salt units in **2b** ranged from about 5 to 15% ($x/(n-x) \simeq 19$–6). A polysalt obtained at a reactant ratio $n(PF_6)/\mathbf{2a}$ of 5:1 typically had the composition **2b**, $x/(n-x) = 10$. Attempts to achieve complete replacement of sulfate by hexafluorophosphate anions in the polysalt failed; even the addition of an excess of hexafluorophosphate (PF_6^-) as large as ten equivalents caused but minor compositional changes in the product polymer.

The polysalts **2b**, as expected, were insoluble in water yet dissolved readily in sulfuric acid and dimethyl sulfoxide (DMSO), although, in the latter solvent, they rapidly degraded by reduction.[8] The solid-state IR spectra exhibited the characteristic ferricenium absorption pattern,[4a,f] although the diagnostically important 900–800 cm^{-1} region[9] was buried in the powerful anion band (ν_3). Depending on the sulfate content, weak to very weak absorption due to the sulfate anion complex was shown at 1210–1180 cm^{-1} (ν_3) and near 590 cm^{-1} (ν_4), the high-frequency position of the former indicating a bidentate bridging function between cationic sites.[10] The spectra also displayed a very faint signal at 500–490 cm^{-1}, i.e. at a frequency where neutral ferrocene and, indeed, the parent polymer



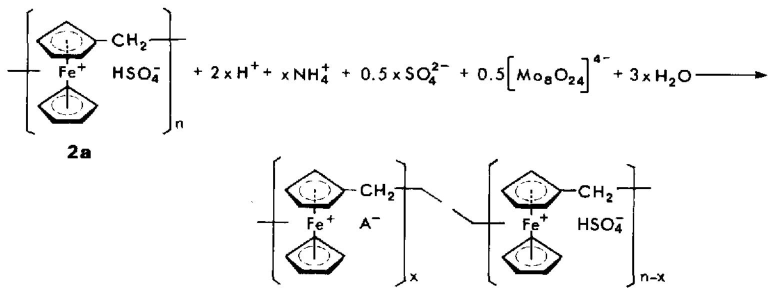
[2]

1 both absorb strongly (ν_{21}, ν_{11}).[9] However, the same absorption appears weakly in the spectrum of pure ferricenium hexafluorophosphate[4f] and, hence, cannot in the present case be adduced as evidence of the presence of units of 1. In the electronic absorption spectrum (H_2SO_4) the polysalts gave the typical $e_1' \rightarrow e_2'$ ferricenium ligand-to-metal CT band[11] at 620 nm.

With the precipitability of the ferricenium polycation thus demonstrated, a series of experiments were performed with the aim of precipitating molybdate polysalts. Aqueous sulfuric acid solutions of **2a**, 0.14–0.17 mol dm^{-3}, prepared as described above, were treated with an excess (1.5–4 molar equivalents) of ammonium molybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$). The polymeric products precipitated in 98–100% yield. Not unexpectedly in view of the known behavior of molybdates in acidic phase,[12] the polysalts turned out to be of rather variable composition even when experimental conditions were kept constant as far as practicable. No reproducible correlations between reactant ratio and anion composition in the products were noticeable as long as two or more molar equivalents of molybdate were used. In a typical anion exchange experiment conducted in an $n(Mo_7)/$**2a** reactant ratio of 2, the precipitated product conformed in elemental composition to a polysalt possessing protonated heteropolyanions with trapped sulfate ($SO_4{}^{2-}$) approximately of the type $[H_8Mo_8O_{28}(SO_4)_3]^{4-}$, and the overall structure was best represented by **2c** [$x/(n(x) = 10$], which includes ammonium cation (Eqn [3]). In highly acidic environments the molybdate anion is known[12] to exist predominantly as an octamolybdate complex, generally protonated to an appreciable extent. The structure **2c** as formulated includes a fraction of units of **2a** as similarly found in the poly(hexafluorophosphate) model polysalt **2b**. We concede the somewhat arbitrary choice of a given ratio $x/(n-x)$. The rather wide experimental error limits of the elemental analyses (see the Experimental section) will indeed tolerate an appreciable variation of the contents of units of **2a** to be calculated from the analytical data. However, it stands to reason that the incorporation of such units in **2c** (and, equally so, in **2d**; *vide infra*) will not be less, on balance, than in the model polysalt **2b** possessing the appreciably less bulky hexafluorophosphate ($PF_6{}^-$) anion component. Values of the ratio $x/(n-x)$ ranging from about 15 to 5 have been assessed by microanalysis for numerous other polysalts **2c** prepared in this study.

The variously composed polymolybdates were almost completely insoluble in water but dissolved readily in sulfuric acid. In the IR spectra the characteristic 850 cm^{-1} ferricenium band emerged only partially from the dominant anion absorption pattern, specifically the strong bands at 950 and 740 cm^{-1}; the 900–800 cm^{-1} region, hence, was not diagnostically useful for an assessment of the degree of oxidation. However, the region of 500–480 cm^{-1} characteristic of neutral ferrocene compounds[9] is essentially unencumbered by anion absorption. In the spectra of the great majority of samples of **2c** no absorption, or at best a very faint shoulder, was detected in that region, indicating these polysalts to be substantially or entirely free from neutral, i.e. non-oxididized, units of 1. This was confirmed by the Mössbauer spectra, which generally lacked any quadrupole-split doublets due to the neutral ferrocene complex[13,14] (*vide infra*). All samples absorbed in the sulfate IR frequency regions cited above, although there was partial overlap by an anion band near 1200 cm^{-1}.

In the last set of experiments phosphomolybdic



2a

2c

[3]

$A^- = NH_4^+ [H_8Mo_8O_{27}(SO_4)_3]^{4-}_{0.5} \cdot 2.5H_2O$

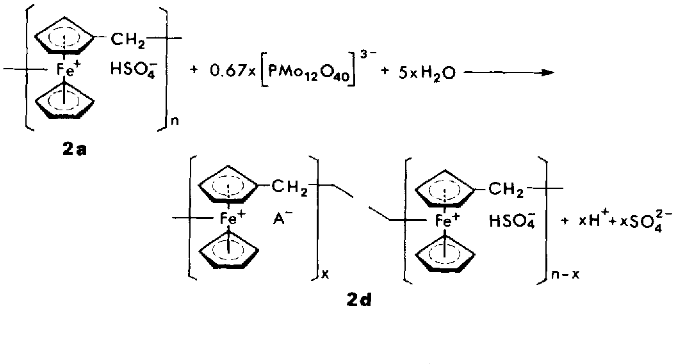
acid was employed as the molybdenum-containing anion donor. This heteropolyacid, commonly represented as $H_3PO_4 . 12MoO_3 . xH_2O$ or $H_3[PMo_{12}O_{40}] . xH_2O$, was treated with the aqueous acidic (0.14–0.17 mol dm^{-3}) solution of ferricenium polysalt **2a** as in the preceding series of experiments, molar ratios of heteropolyacid to repeat unit of **2a** being 1.5–4. Phosphomolybdate polysalts, containing the $[PMo_{12}O_{40}]^{3-}$ anion complex, precipitated immediately in quantitative yields. Overall polymer compositions showed little dependence on reactant ratios provided that the phosphomolybdic acid was used in excess over equimolarity, and the heteropolyanion composition remained remarkably constant irrespective of the reaction conditions, molybdenum/phosphorus atomic ratios generally being in the narrow range of 11.2–12.0 (calcd. for phosphomolybdic acid: 12.0). As in the previous case, the products proved to be copolymers containing a minor fraction, typically about 10%, of units of **2a**. A representative polysalt, obtained at an $n(Mo_{12})/$**2a** reactant ratio of 2:1, corresponded in elemental composition to a poly(phosphomolybdate) of type **2d**, $x/(n-x) = 10$ (Eqn [4]).

The poly(phosphomolybdates), irrespective of compositional variations, dissolved completely in sulfuric acid and partially in DMSO, yet only sparingly in water. The IR spectra, similar to those of **2c**, were dominated by the intense absorption pattern of the heteropolyanion. The 850 cm^{-1} ferricenium band was partially merged with the envelopes of the strong anion band at 865 cm^{-1} and the even stronger one near 800 cm^{-1}, burying the region centered at 820 cm^{-1}; hence, this frequency region could not be utilized for an assessment of possible contents of units **1**. Similarly useless for this diagnostic purpose was the 500–480 cm^{-1} region, which was covered by the envelope of an anion band at 505 cm^{-1}, masking any weak ferrocene band potentially present in that region. Well in accord with the determined sulfur contents of the polysalts, broad sulfate absorptions appeared in weak to moderate intensity near 1200 and 600 cm^{-1} as shown by **2b** and **2c**.

The question of possible inclusions of units of **1** in the polysalts **2d** was answered by Mössbauer spectroscopy. The 295K spectra displayed a single resonance signal appearing as a broad singlet at $\delta = 0.45 \pm 0.02$ mm s^{-1} (relative to α-iron foil), i.e. at the velocity position typical of the ferricenium system,[13] and there was generally no indication of the doublet resonance, typically with $\delta \simeq 0.43$–0.50 mm s^{-1} and $\Delta E_q \simeq 2.30$–2.50 mm s^{-1}, characterizing the neutral ferrocene system.[13,15] This suggests that units of **1** were either entirely absent or else, if present, occurred in negligible proportions in the poly(phosphomolybdates) of this study.

The results demonstrate the feasibility of oxidizing inherently hydrophobic ferrocene-containing polymers to polysalts that are soluble in aqueous acidic medium and which can be precipitated in the presence of bulky anion complexes. The aqueous-phase preparative approach chosen represents a useful complement to the previously reported[1] synthesis of polyferricenium salts prepared in an organic phase.

The target polymers **2c** and **2d** are ionic as desired and possess the required insolubility in water. The polycationic backbone, as shown in preliminary screening work, degrades slowly, over periods of six months or more, by cleavage of the iron–cyclopentadienyl ring bond (weakened in the ferricenium complex relative to ferrocene), releasing mobile and bioavailable iron(II) (Fe^{2+})



[4]

$$A^- = H^+[PMo_{12}O_{40}]^{3-}_{0.67} \cdot 5H_2O$$

ion, which may undergo subsequent oxidation in the soil. As the ferricenium sites in the polymer chain thus vanish gradually, so do the iso- or hetero-polyanion cluster counter-ions. It must be assumed, however, that other delivery mechanisms, such as anion exchange, add to the overall release rate of these counter-ions despite their considerable bulkiness, thus resulting in somewhat earlier depletion of molybdenum than of iron. Polymers **2c** and **2d** are currently being evaluated for phytotoxicity in *Zea mays* plant growth studies, and long-range degradation work in variable soils will have to be performed in the future for an assessment of relative release kinetics.

EXPERIMENTAL

General

IR spectra were taken on KBr pellets and were recorded over the range of 4000–200 cm^{-1}. Electronic absorption spectra were recorded on 98% H_2SO_4 solutions in the range 700–600 nm. Mössbauer spectra were obtained in the transmission mode (cobalt/rhodium source; chemical shifts, δ, in mm s^{-1} referenced against α-iron foil at room temperature). Number-average molecular masses, $\bar{M}_n$, were determined by vapor-pressure osmometry in benzene at 30°C. Microanalyses were performed by Robertson Laboratory, Inc., Florham Park, NJ, Galbraith Laboratories, Inc., Knoxville, Tenn., and in the Microanalytical Laboratory of the University of the Witwatersrand. Appreciable scattering of results was encountered with fluorine (±1.6%), iron (±0.8%), molybdenum (±1.0%), phosphorus (±0.9%), and sulfur (±0.8%); these elements were determined in duplicate or triplicate, and the results are reported as averages. Analytical samples were additionally dried for 2 days at 80–85°C/0.1 torr. Water used in the experimental work was deionized, and the solvents used for solubility testing were deoxygenated by purging with nitrogen. All molar concentration data given for polymeric reactants are base molar, i.e. they refer to the molarity of polymer repeat unit.

(a) Poly[ferrocene-1,2(1,3:1,1')diyl-methylene] (1)

The linear ferrocenylenemethylene polymer was prepared by the zinc chloride/hydrogen chloride-catalyzed polycondensation of *N*,*N*-dimethylaminomethylferrocene (experiment 3 of Ref. 2). The crude polymer was reprecipitated stepwise from de-aerated toluene solution by deoxygenated methanol, and the major fraction, $\bar{M}_n = 2800$ ($n = 14$), was used for the present work.

Analysis: Calc. for $(C_{11}H_{10}Fe)_n$ (**1**): Fe, 28.20. Found: Fe, 28.03%. IR (substituted ferrocene system) (cm^{-1}): 1105m, 1028(d)m, 1000m, 815s, 485s.

(b) Poly[ferricene-1,2(1,3:1,1')diyl-methylene hydrogen sulfate] (2a) by oxidation of 1

In a preliminary experiment, polymer **1** (1.00g) was dissolved with vigorous stirring in 98% H_2SO_4 (3.5 cm^3). A brisk stream of oxygen was passed through the solution for 2 min, which was then stirred for 25 min at ambient temperature and filtered through fritted glass. The blackish solid residue of partly degraded material was washed successively with H_2SO_4 (0.5 cm^3), water (10 cm^3), and methanol (10 cm^3) and was rapidly dried at 120°C/0.01 torr. A mass of 0.18 g (18% of the quantity of **1** employed) was determined for this residue.

Analysis: Found: C, 52.76; H, 4.32; Fe 15.76%.

In several repeat runs, residual masses ranged from about 10 to 20%, but generally were 16 ±3% of that of the starting material. On the basis of these results, a 20% excess over the required quantity of **1** was routinely employed in all oxidation experiments to compensate for the loss of residue, and the exact concentration of polymer solute in the filtrate was calculated from the accurate mass of residue determined. A representative oxidation experiment is described below.

An oxygen-saturated solution of **1**, 2.38 g (12 mmol), in 98% H_2SO_4 (6 cm^3) was prepared as described in the preceding paragraph. After brief (25 min) stirring at ambient temperature the dark green solution of the generated **2a** (not isolated) was purged with nitrogen for removal of oxygen and was filtered as above. The filtrate, combined with the acid washings (1.5 cm^3), was poured slowly into vigorously stirred ice water presaturated with nitrogen (50 cm^3, including the water washings, 20 cm^3, of the residue). The bluish solution was topped up with water under nitrogen to give a master solution of 70 cm^3 volume. From the dry mass of the filtration residue, 0.42 g, ignoring any sulfate contents in that residual material, the effectively dissolved mass of **1** was taken to be 1.96 g (9.9 mmol) corresponding to a concentration of 0.141 mol dm^{-3}. Hence, the solute content of 7.1 cm^3 of this master solution approximated to 1 mmol.

(c) Poly{[ferricene-1,2(1,3:1,1′)diyl-methylene hexafluorophosphate]-co-[ferricene-1,2(1,3:1,1′)diyl-methylene hydrogen sulfate]} (2b)

Into the stirred solution of NH_4PF_6 (815 mg, 5 mmol) in water (3 cm^3) saturated with nitrogen, was slowly poured a 7.1 cm^3 portion (1 mmol) of the master solution of **2a** obtained as described in the preceding paragraph. The mixture was stirred for 2 h at 20–25°C in a stoppered flask. The precipitated poly(hexafluorophosphate) **2b** was collected by filtration, washed well with ice water and diethyl ether, and was dried for two days at ambient temperature over P_4O_{10} under reduced pressure, followed by 24 h at 50°C/0.1 torr. The bluish-black, powdery solid, 350 mg (94%), dissolved smoothly in 98% H_2SO_4 (blue solution) and in DMSO (greenish solution, rapidly turning brown with separation of brownish particles), but was insoluble in water.*

Analysis: Calc. for $(C_{12.1}H_{11.1}F_6Fe_{1.1}O_{0.4}PS_{0.1})_n$ (**2b**, $x/(n-x)=10$): C, 39.01; H, 3.00; F, 30.60; Fe, 16.49; P, 8.31; S, 0.86. Found: C, 38.90; H, 3.40; F, 29.71; Fe, 15.27; P, 7.93; S, 1.07%.

Duplicate anion exchange experiments gave polymers with contents of carbon, fluorine, iron, phosphorus and sulfur varying within the respective ranges of 37–42, 26–31, 13–17, 6–9, and 0.7–1.5%. Similar compositions were determined for polysalts obtained at $n(PF_6)/$**2a** ratios of three to four. For comparison, for a product prepared at the extreme ratio of 10, analysis found: C, 37.33; H, 3.01; Fe, 12.20; P, 10.33; S, 1.13.

(d) Poly{[ferricene-1,2(1,3:1,1′)diyl-methylene ammmonium hemi(octahydrogen trisulfato-octamolybdate)]-co-[ferricene-1,2(1,3:1,1′)diyl-methylene hydrogen sulfate]} (2c)

A 7.1 cm^3 portion (1 mmol) of the master solution of **2a** prepared as described under (a), above, was slowly poured into the stirred, nitrogen-saturated solution of $(NH_4)_6Mo_7O_{24}.4H_2O$, (2.47 g, 2 mmol), in water (15 cm^3; heating required for dissolution), and stirring of the mixture at ambient temperature in a stoppered flask was continued for 2 h. The bluish-black precipitate of **2c** was filtered off, washed with ice water and diethyl ether, and dried as described for the preceding experiments. Yield 1.02 g (98%). The polymer was completely soluble in 98% H_2SO_4 (deep blue)† and partly soluble in DMSO (light blue); it dissolved sparingly in water.

Analysis: Calc. for $(C_{12.1}H_{24.1}Fe_{1.1}Mo_4NO_{22.4}S_{1.6})_n$ (**2c**, $x/(n-x)=10$): C, 13.99; H, 2.34; Fe, 5.92; Mo, 36.95; N, 1.35; O, 34.51; S, 4.94. Found: C, 13.29; H, 2.20; Fe, 5.11; Mo, 35.87; N, 1.30; O, 35.26; S, 4.55%.

Analyses obtained for polymolybdates precipitated in repeat experiments gave the following variations: C, 11–17; Fe, 4–6; Mo, 34–40; N, 1–2, O, 33–35; S, 3–6%. Higher reactant ratios, $n(Mo_7)/$**2a** = 3–4, did not lead to substantially different elemental product compositions.

(e) Poly{[ferricene-1,2(1,3:1,1′)diyl-methylene hydrogen phosphododecamolybdate]-co-[ferricene-1,2(1,3:1,1′)diyl-methylene hydrogen sulfate]} (2d)

A solution of $H_3[PMo_{12}O_{40}].xH_2O$ (3.83 g, 2 mmol; x arbitrarily taken to be 5) in water (4.5 cm^3) was treated with a 7.1 cm^3 portion (1 mmol) of the master solution of **2a** prepared as described under (a), above. The bluish-black precipitate, collected, washed and dried as in the preceding experiments, weighed 1.52 g (99%) and showed the same solubility behavior as reported above for **2c**.

Analysis: Calc. for $(C_{12.1}H_{22.1}Fe_{1.1}Mo_8O_{32.07}P_{0.67}S_{0.1})_n$ (**2d**, $x/(n-x)=10$): C, 9.48; H, 1.45; Fe, 4.01; Mo, 50.05; P, 1.35; S, 0.21. Found: C, 9.90; H, 1.90; Fe, 4.05; Mo, 50.65; P, 1.40; S, 0.32%.

The elemental contents analytically determined for polysalts obtained in repeat experiments, as well as in runs performed at molar reactant ratios of 1.5, 3, and 4, varied within the following ranges: C, 9–13; Fe, 3.8–5.8; Mo, 47–52; P, 1.3–1.5; S, 0.2–0.5%. An experiment conducted at the abnormally high $n(Mo_7)/$**2a** ratio of 10 gave a polysalt with the analysis: Found: C, 13.91; H, 1.57; Fe, 5.30; Mo, 48.08%.

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14. Polymers obtained under conditions of incomplete oxygenation or insufficiently long stirring periods occasionally showed an additional doublet with $\delta \simeq 0.6$–$1.1\,\mathrm{mm\,s}^{-1}$ and $\Delta E_q \simeq 2.8$–$3.3\,\mathrm{mm\,s}^{-1}$ in the 295K Mössbauer spectrum. These signals are associated with iron(II) species in the $S=2$ spin state and indicate the presence of ferrocenonium (i.e. iron-protonated) units of **1** generated in the highly acidic medium as potential precursors of **2a**. Stable iron-protonated salts derived from certain (geometrically favored) 1- and 2-ferrocenophanes, giving Mössbauer resonances of the very same type here observed, were recently reported.[14a,b] It is of interest to note that we have rarely observed these iron(II)-type Mössbauer doublets in the spectra of poly(phosphomolybdates), and this may be due to the strong oxidizing action exerted by phosphomolybdic acid, preventing the build-up of (non-oxidized) ferrocenonium units. The phenomenon of Fe-H bond formation in ferrocene polymers dererves further attention. (a) Clemence, M, Roberts, R M G and Silver, J *J. Organomet. Chem.*, 1983, 243: 461; (b) Watanabe, M, Motoyama, I and Sano, H *J. Radioanal. Nucl. Chem. Lett.*, 1985, 96: 585
15. Good, M L, Buttone, J and Foyt, D *Ann. N.Y. Acad. Sci.*, 1974, 239: 193

Note added in proof

*Long-term storage (6–12 months) at room temperature caused significant reduction in sulphuric acid solubility.

†It was less completely soluble after 6–12 months at room temperature.